

## PATTERN FORMATION METHOD

### BACKGROUND OF THE INVENTION

The present invention relates to a pattern formation method for use in fabrication  
5 process and the like for semiconductor devices.

In accordance with the increased degree of integration of semiconductor  
integrated circuits and downsizing of semiconductor devices, there are increasing demands  
for further rapid development of lithography technique. Currently, pattern formation is  
carried out through photolithography using exposing light of a mercury lamp, KrF excimer  
10 laser, ArF excimer laser or the like, and use of F<sub>2</sub> laser lasing at a shorter wavelength is  
being examined. However, since there remain a large number of problems in exposure  
systems and resist materials, photolithography using exposing light of a shorter wavelength  
has not been put to practical use.

In these circumstances, immersion lithography has been recently proposed for  
15 realizing further refinement of patterns by using conventional exposing light (M. Switkes  
and M. Rothschild, "Immersion lithography at 157 nm", J. Vac. Sci. Technol., B19, 2353  
(2001)).

In the immersion lithography, a region in an exposure system sandwiched between  
a projection lens and a resist film formed on a wafer is filled with a solution having a  
20 refractive index  $n$ , and therefore, the NA (numerical aperture) of the exposure system has a  
value  $n \cdot NA$ . As a result, the resolution of the resist film can be improved.

Now, a first conventional pattern formation method using the immersion  
lithography will be described with reference to FIGS. 8A through 8D.

First, a positive chemically amplified resist material having the following  
25 composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

5 Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 8A, the aforementioned chemically amplified resist material is applied on a substrate 1 so as to form a resist film 2 with a thickness of 0.35  $\mu\text{m}$ .

Then, as shown in FIG. 8B, while supplying water 3A onto the resist film 2, pattern exposure is carried out by irradiating the resist film 2 with exposing light 4 of ArF  
10 excimer laser with NA of 0.65 through a mask 5. Although a projection lens for condensing the exposing light 4 having passed through the mask 5 on the surface of the resist film 2 is not shown in FIG. 8B, a region sandwiched between the projection lens and the resist film 2 is filled with the water 3A. Thus, an exposed portion 2a of the resist film 2 becomes soluble in an alkaline developer because an acid is generated from the acid  
15 generator therein while an unexposed portion 2b of the resist film 2 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 8C, the resist film 2 is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline  
20 developer). In this manner, a resist pattern 6A made of the unexposed portion 2b of the resist film 2 can be obtained as shown in FIG. 8D.

Next, a second conventional pattern formation method using the immersion lithography will be described with reference to FIGS. 9A through 9D.

First, a positive chemically amplified resist material having the following  
25 composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

5 Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 9A, the aforementioned chemically amplified resist material is applied on a substrate 1 so as to form a resist film 2 with a thickness of 0.20  $\mu\text{m}$ .

Then, as shown in FIG. 9B, while supplying perfluoropolyether 3B onto the resist film 2, pattern exposure is carried out by irradiating the resist film 2 with exposing light 4 of F<sub>2</sub> laser with NA of 0.60 through a mask 5. Although a projection lens for condensing the exposing light 4 having passed through the mask 5 on the surface of the resist film 2 is not shown in FIG. 9B, a region sandwiched between the projection lens and the resist film 2 is filled with the perfluoropolyether 3B. Thus, an exposed portion 2a of the resist film 2 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 2b of the resist film 2 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 9C, the resist film 2 is baked with a hot plate at a temperature of 100°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 6B made of the unexposed portion 2b of the resist film 2 can be obtained as shown in FIG. 9D.

As shown in FIGS. 8D and 9D, however, each of the resist patterns 6A and 6B formed by the first and second conventional pattern formation methods is in a defective T-top shape.

25 Since the positive chemically amplified resist material is used in each of the first

and second conventional pattern formation methods, the resist pattern **6A** or **6B** is in the T-top shape. When a negative chemically amplified resist material is used instead, the resultant resist pattern is in a defective shape with round shoulders.

When a resist pattern in such a defective shape is used for etching a target film,  
5 the resultant pattern is also in a defective shape, which disadvantageously lowers the productivity and the yield in the fabrication process for semiconductor devices.

### **SUMMARY OF THE INVENTION**

In consideration of the aforementioned conventional problem, an object of the  
10 invention is forming a resist pattern in a good shape by the immersion lithography.

In order to achieve the object, the first pattern formation method of this invention includes the steps of forming a resist film of a chemically amplified resist material including a base polymer, an acid generator for generating an acid through irradiation with light and lactone; performing pattern exposure by selectively irradiating the resist film with  
15 exposing light while supplying a solution onto the resist film; and forming a resist pattern by developing the resist film after the pattern exposure.

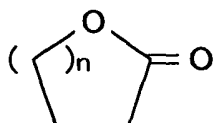
The second pattern formation method of this invention includes the steps of forming a resist film of a chemically amplified resist material including a base polymer, an acid generator for generating an acid through irradiation with light and a polymer  
20 containing lactone; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying a solution onto the resist film; and forming a resist pattern by developing the resist film after the pattern exposure.

In the first or second pattern formation method, a carbonyl group included in the lactone exhibits polarity, and therefore, the acid generated from the acid generator is held  
25 by the carbonyl group in the resist film. Accordingly, the acid can be prevented from

being deactivated in an exposed portion of the resist film, so that the resist pattern can be formed in a good shape. As a result, since a target film can be etched by using the resist pattern in a good shape, the resultant pattern can be in a good shape. Thus, the productivity and the yield in the fabrication process for semiconductor devices can be improved.

In the first or second pattern formation method, the lactone means a cyclic compound having a  $\text{-CO-O-}$  group in a ring of hydroxycarboxylic acid as represented by Chemical Formula 1, and specific examples of the lactone are mevalonic lactone,  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone and  $\delta$ -valerolactone.

Chemical Formula 1:



wherein n is an integer of 1 through 4.

In the second pattern formation method, the polymer for containing the lactone may be poly(acrylic ester) or poly(methacrylic ester).

The third pattern formation method of this invention includes the steps of forming a resist film of a chemically amplified resist material including a base polymer, an acid generator for generating an acid through irradiation with light and carbohydrate lactone; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying a solution onto the resist film; and forming a resist pattern by developing the resist film after the pattern exposure.

In the third pattern formation method, a carbonyl group included in the lactone exhibits polarity, and therefore, the acid generated from the acid generator is held by the carbonyl group in the resist film. Accordingly, the acid can be prevented from being deactivated in an exposed portion of the resist film, so that the resist pattern can be formed

in a good shape. As a result, since a target film can be etched by using the resist pattern in a good shape, the resultant pattern can be in a good shape. Thus, the productivity and the yield in the fabrication process for semiconductor devices can be improved.

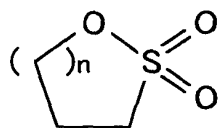
In the third pattern formation method, the carbohydrate lactone may be D-  
5 gluconic acid  $\delta$ -lactone,  $\beta$ -D-glucofurannurone acid  $\gamma$ -lactone or L-mannal acid di- $\gamma$ -lactone.

The fourth pattern formation method of this invention includes the steps of forming a resist film of a chemically amplified resist material including a base polymer, an acid generator for generating an acid through irradiation with light and sultone; performing  
10 pattern exposure by selectively irradiating the resist film with exposing light while supplying a solution onto the resist film; and forming a resist pattern by developing the resist film after the pattern exposure.

In the fourth pattern formation method, a sulfonyl group included in the sultone exhibits polarity, and therefore, the acid generated from the acid generator is held by the  
15 sulfonyl group in the resist film. Accordingly, the acid can be prevented from being deactivated in an exposed portion of the resist film, so that the resist pattern can be formed in a good shape. As a result, since a target film can be etched by using the resist pattern in a good shape, the resultant pattern can be in a good shape. Thus, the productivity and the yield in the fabrication process for semiconductor devices can be improved.

20 In the fourth pattern formation method, the sultone means a cyclic compound having a  $-\text{SO}_2-\text{O}-$  group in a ring of hydroxysulfonic acid as represented by Chemical Formula 2, and specific examples of the sultone are pentane-2,5-sultone and naphthalene-1,8-sultone.

Chemical Formula 2:



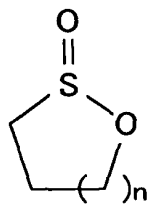
wherein n is an integer of 1 through 4.

The fifth pattern formation method of this invention includes the steps of forming a resist film of a chemically amplified resist material including a base polymer, an acid generator for generating an acid through irradiation with light and sultine; performing  
 5 pattern exposure by selectively irradiating the resist film with exposing light while supplying a solution onto the resist film; and forming a resist pattern by developing the resist film after the pattern exposure.

In the fifth pattern formation method, a sulfonyl group included in the sultine  
 10 exhibits polarity, and therefore, the acid generated from the acid generator is held by the sulfonyl group in the resist film. Accordingly, the acid can be prevented from being deactivated in an exposed portion of the resist film, so that the resist pattern can be formed in a good shape. As a result, since a target film can be etched by using the resist pattern in a good shape, the resultant pattern can be in a good shape. Thus, the productivity and  
 15 the yield in the fabrication process for semiconductor devices can be improved.

In the fifth pattern formation method, the sultine means a cyclic compound having a  $-SO-O-$  group in a ring of hydroxysulfonic acid as represented by Chemical Formula 3, and a specific example of the sultine is 3H-2,1-benzoxathiol=1-oxide.

Chemical Formula 3:



20

wherein n is an integer of 1 through 4.

In each of the first through fifth pattern formation methods, the solution is preferably water.

When water with a large refractive index is used as the solution, a value  $n \cdot NA$  can be definitely increased.

5        In each of the first through fifth pattern formation methods, the solution is preferably perfluoropolyether.

In the case where perfluoropolyether is used as the solution, even if a water-soluble film is formed on the resist pattern, the water-soluble film can be prevented from being dissolved in the solution.

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#### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a partial cross-sectional view of an exposure system commonly used in preferred embodiments of the invention;

15        FIGS. 2A, 2B, 2C and 2D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 1 of the invention;

FIGS. 3A, 3B, 3C and 3D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 2 of the invention;

FIGS. 4A, 4B, 4C and 4D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 3 of the invention;

20        FIGS. 5A, 5B, 5C and 5D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 5 of the invention;

FIGS. 6A, 6B, 6C and 6D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 7 of the invention;

25        FIGS. 7A, 7B, 7C and 7D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 9 of the invention;



FIGS. **8A**, **8B**, **8C** and **8D** are cross-sectional views for showing procedures in a first conventional pattern formation method; and

FIGS. **9A**, **9B**, **9C** and **9D** are cross-sectional views for showing procedures in a second conventional pattern formation method.

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## **DETAILED DESCRIPTION OF THE INVENTION**

Pattern formation methods according to preferred embodiments of the invention will now be described, and first of all, an exposure system used in each embodiment will be described with reference to FIG. 1. It is noted that the exposure system used in the  
10 pattern formation method of each embodiment is not limited to one having the structure shown in FIG. 1 but any of systems capable of realizing the immersion lithography can be used.

As shown in FIG. 1, a projection lens **12** of the exposure system is provided above a resist film **11** formed on a semiconductor substrate **10**, and a solution storage **14** for  
15 storing a solution **13** (with a refractive index  $n$ ) is provided between the projection lens **12** and the resist film **11**. The solution storage **14** is provided with an inlet **14a** for allowing the solution **13** to flow into and an outlet **14b** for allowing the solution **13** to flow out of the solution storage **14**, and the solution **13** having flown into the solution storage **14** through the inlet **14a** is temporarily stored in the solution storage **14** and then flows out  
20 through the outlet **14b**. Accordingly, exposing light **15** passes through a mask **16** having a desired pattern, and is then condensed by the projection lens **12** so as to reach the surface of the resist film **11** through the solution **13**. Therefore, the numerical aperture NA of the exposing light that reaches the surface of the resist film **11** through the solution **13** has a value  $n$  times as large as that attained when the exposing light reaches without passing  
25 through the solution **13**.

## EMBODIMENT 1

A pattern formation method according to Embodiment 1 of the invention will now be described with reference to FIGS. 2A through 2D.

First, a positive chemically amplified resist material having the following  
5 composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Lactone:  $\gamma$ -butyrolactone ... 0.06 g

10 Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 2A, the aforementioned chemically amplified resist material is applied on a substrate 101 so as to form a resist film 102 with a thickness of 0.35  $\mu\text{m}$ .

15 Then, as shown in FIG. 2B, while supplying, onto the resist film 102, water 103 (having a refractive index  $n$  of 1.44) that is circulated and temporarily stored in the solution storage 14 (shown in FIG. 1), pattern exposure is carried out by irradiating the resist film 102 with exposing light 104 of ArF excimer laser with NA of 0.65 through a mask not shown. In FIG. 2B, a reference numeral 106 denotes a projection lens disposed  
20 above the resist film 102. Thus, an exposed portion 102a of the resist film 102 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 102b of the resist film 102 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 2C, the resist film 102 is baked with  
25 a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is

developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **105** made of the unexposed portion **102b** of the resist film **102** and having a line width of 0.09  $\mu\text{m}$  can be formed in a good shape as shown in FIG. **2D**.

5            In Embodiment 1, since a carbonyl group included in the lactone exhibits polarity, the acid generated from the acid generator is held by the carbonyl group in the resist film **102**. Accordingly, the acid can be prevented from being deactivated in the exposed portion **102a** of the resist film **102**, so that the resist pattern **105** can be formed in a good shape.

## 10    EMBODIMENT 2

A pattern formation method according to Embodiment 2 of the invention will now be described with reference to FIGS. **3A** through **3D**.

First, a negative chemically amplified resist material having the following composition is prepared:

15            Base polymer: poly((norbornene-5-methylenecarboxylic acid) – (maleic anhydride)) (wherein norbornene-5-methylenecarboxylic acid : maleic anhydride = 50 mol% : 50 mol%)    ...    2 g

Crosslinking agent: 1,3,5-N-(trihydroxymethyl)melamine    ...    0.4 g

Lactone:  $\delta$ -valerolactone    ...    0.07 g

20            Acid generator: triphenylsulfonium nonaflate    ...    0.05 g

Solvent: propylene glycol monomethyl ether acetate    ...    20 g

Next, as shown in FIG. **3A**, the aforementioned chemically amplified resist material is applied on a substrate **201** so as to form a resist film **202** with a thickness of 0.35  $\mu\text{m}$ .

25            Then, as shown in FIG. **3B**, while supplying, onto the resist film **202**, water **203**

that is circulated and temporarily stored in the solution storage **14** (shown in FIG. 1), pattern exposure is carried out by irradiating the resist film **202** with exposing light **204** of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion **202a** of the resist film **202** becomes insoluble in an alkaline developer due to the function of the crosslinking agent because an acid is generated from the acid generator therein while an unexposed portion **202b** of the resist film **202** remains soluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 3C, the resist film **202** is baked with a hot plate at a temperature of 120°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **205** made of the exposed portion **202a** of the resist film **202** and having a line width of 0.09  $\mu\text{m}$  can be formed in a good shape as shown in FIG. 3D.

In Embodiment 2, since a carbonyl group included in the lactone exhibits polarity, the acid generated from the acid generator is held by the carbonyl group in the resist film **202**. Accordingly, the acid can be prevented from being deactivated in the exposed portion **202a** of the resist film **202**, so that the resist pattern **205** can be formed in a good shape.

In Embodiment 1 or 2, the lactone can be, for example, mevalonic lactone,  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone or  $\delta$ -valerolactone.

Also, the mixing ratio of the lactone in the chemically amplified resist material is several wt% and may be appropriately changed.

### EMBODIMENT 3

A pattern formation method according to Embodiment 3 of the invention will now be described with reference to FIGS. 4A through 4D.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Polymer including lactone: poly(mevalonic lactone methacrylate) ... 0.04 g

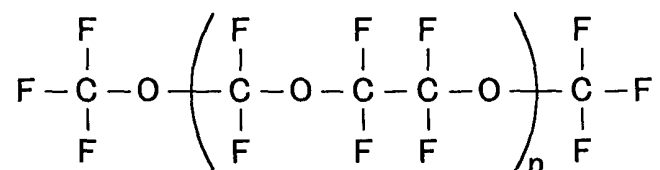
Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 4A, the aforementioned chemically amplified resist material is applied on a substrate 301 so as to form a resist film 302 with a thickness of 0.20 μm.

Then, as shown in FIG. 4B, while supplying, onto the resist film 302, a nonaqueous solution 303 of perfluoropolyether (having a refractive index *n* of 1.37) that is represented by Chemical Formula 4 and is circulated and temporarily stored in the solution storage 14 (shown in FIG. 1), pattern exposure is carried out by irradiating the resist film 302 with exposing light 304 of F<sub>2</sub> laser with NA of 0.60 through a mask not shown. Thus, an exposed portion 302a of the resist film 302 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 302b of the resist film 302 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

Chemical Formula 4:



After the pattern exposure, as shown in FIG. 4C, the resist film 302 is baked with

a hot plate at a temperature of 100°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **305** made of the unexposed portion **302b** of the resist film **302** and having a line width of 0.06  $\mu\text{m}$  can be formed in a good shape as shown in FIG. **4D**.

In Embodiment 3, since a carbonyl group included in the lactone exhibits polarity, the acid generated from the acid generator is held by the carbonyl group in the resist film **302**. Accordingly, the acid can be prevented from being deactivated in the exposed portion **302a** of the resist film **302**, so that the resist pattern **305** can be formed in a good shape.

#### EMBODIMENT 4

A pattern formation method according to Embodiment 4 of the invention will now be described. Embodiment 4 is different from Embodiment 3 merely in using a negative chemically amplified resist material, and therefore, the chemically amplified resist material alone will be herein described.

Base polymer: poly((norbornene-5-methylenecarboxylic acid) – (maleic anhydride)) (wherein norbornene-5-methylenecarboxylic acid : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Crosslinking agent: 1,3,5-N-(trihydroxymethyl)melamine ... 0.7 g

Polymer including lactone: poly( $\gamma$ -valerolactone methacrylate) ... 0.05 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

In Embodiment 3 or 4, the lactone can be, for example, mevalonic lactone,  $\gamma$ -butyrolactone,  $\gamma$ -valerolactone or  $\delta$ -valerolactone, and examples of the polymer for including lactone are poly(acrylic ester) and poly(methacrylic ester).

Also, the mixing ratio of the polymer including lactone in the chemically amplified resist material is several wt% and may be appropriately changed.

#### EMBODIMENT 5

A pattern formation method according to Embodiment 5 of the invention will now  
5 be described with reference to FIGS. 5A through 5D.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50  
10 mol% : 50 mol%) ... 2 g

Carbohydrate lactone: D-gluconic acid  $\delta$ -lactone ... 0.07 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 5A, the aforementioned chemically amplified resist  
15 material is applied on a substrate 401 so as to form a resist film 402 with a thickness of 0.35  $\mu\text{m}$ .

Then, as shown in FIG. 5B, while supplying, onto the resist film 402, water 403 (with a refractive index  $n$  of 1.44) that is circulated and temporarily stored in the solution storage 14 (shown in FIG. 1), pattern exposure is carried out by irradiating the resist film  
20 402 with exposing light 404 of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion 402a of the resist film 402 becomes insoluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 402b of the resist film 402 remains soluble in an alkaline developer because no acid is generated from the acid generator therein.

25 After the pattern exposure, as shown in FIG. 5C, the resist film 402 is baked with

a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 405 made of the unexposed portion 402b of the resist film 402 and having a line width of 0.09 μm can be formed in a good shape as shown in FIG. 5D.

In Embodiment 5, since a carbonyl group included in the lactone exhibits polarity, the acid generated from the acid generator is held by the carbonyl group in the resist film 402. Accordingly, the acid can be prevented from being deactivated in the exposed portion 402a of the resist film 402, so that the resist pattern 405 can be formed in a good shape.

#### EMBODIMENT 6

A pattern formation method according to Embodiment 6 of the invention will now be described. Embodiment 6 is different from Embodiment 5 merely in using a negative chemically amplified resist material, and therefore, the chemically amplified resist material alone will be herein described.

Base polymer: poly((norbornene-5-methylenecarboxylic acid) – (maleic anhydride)) (wherein norbornene-5-methylenecarboxylic acid : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Crosslinking agent: 1,3,5-N-(trihydroxymethyl)melamine ... 0.4 g

Carbohydrate lactone: β-D-glucofurannurone acid γ-lactone ... 0.06 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

In Embodiment 5 or 6, the carbohydrate lactone can be, for example, D-gluconic acid δ-lactone, β-D-glucofurannurone acid γ-lactone, L-mannal acid di-γ-lactone or the like.

Also, the mixing ratio of the carbohydrate lactone in the chemically amplified



resist material is several wt% and may be appropriately changed.

#### EMBODIMENT 7

A pattern formation method according to Embodiment 7 of the invention will now be described with reference to FIGS. 6A through 6D.

5 First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

10 Sultone: pentane-2,5-sultone ... 0.1 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 6A, the aforementioned chemically amplified resist material is applied on a substrate 501 so as to form a resist film 502 with a thickness of  
15 0.20  $\mu\text{m}$ .

Then, as shown in FIG. 6B, while supplying, onto the resist film 502, a nonaqueous solution 503 of perfluoropolyether (having a refractive index  $n$  of 1.37) that is circulated and temporarily stored in the solution storage 14 (shown in FIG. 1), pattern exposure is carried out by irradiating the resist film 502 with exposing light 504 of  $\text{F}_2$  laser  
20 with NA of 0.60 through a mask not shown. Thus, an exposed portion 502a of the resist film 502 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 502b of the resist film 502 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

25 After the pattern exposure, as shown in FIG. 6C, the resist film 502 is baked with

a hot plate at a temperature of 100°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **505** made of the unexposed portion **502b** of the resist film **502** and having a line width of 0.06 μm can be formed in a good shape as shown in FIG. **6D**.

In Embodiment 7, since a sulfonyl group included in the sultone exhibits polarity, the acid generated from the acid generator is held by the sulfonyl group in the resist film **502**. Accordingly, the acid can be prevented from being deactivated in the exposed portion **502a** of the resist film **502**, so that the resist pattern **505** can be formed in a good shape.

#### EMBODIMENT 8

A pattern formation method according to Embodiment 8 of the invention will now be described. Embodiment 8 is different from Embodiment 7 merely in using a negative chemically amplified resist material, and therefore, the chemically amplified resist material alone will be herein described.

Base polymer: poly((norbornene-5-methylenecarboxylic acid) – (maleic anhydride)) (wherein norbornene-5-methylenecarboxylic acid : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Crosslinking agent: 1,3,5-N-(trihydroxymethyl)melamine ... 0.4 g

Sultone: naphthalene-1,8-sultone ... 0.06 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

In Embodiment 7 or 8, the sultone can be, for example, pentane-2,5-sultone, naphthalene-1,8-sultone or the like.

Also, the mixing ratio of the sultone in the chemically amplified resist material is

several wt% and may be appropriately changed.

#### EMBODIMENT 9

A pattern formation method according to Embodiment 9 of the invention will now be described with reference to FIGS. 7A through 7D.

5 First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

10 Sultine: 3H-2,1-benzoxathiol=1-oxide ... 0.05 g

Acid generator: triphenylsulfonium nonaflate ... 0.05 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 7A, the aforementioned chemically amplified resist material is applied on a substrate 601 so as to form a resist film 602 with a thickness of  
15 0.35  $\mu\text{m}$ .

Then, as shown in FIG. 7B, while supplying, onto the resist film 602, water 603 (with a refractive index  $n$  of 1.44) that is circulated and temporarily stored in the solution storage 14 (shown in FIG. 1), pattern exposure is carried out by irradiating the resist film 602 with exposing light 604 of ArF excimer laser with NA of 0.65 through a mask not  
20 shown. Thus, an exposed portion 602a of the resist film 602 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 602b of the resist film 602 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 7C, the resist film 602 is baked with  
25 a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is

developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 605 made of the unexposed portion 602b of the resist film 602 and having a line width of 0.09  $\mu\text{m}$  can be formed in a good shape as shown in FIG. 7D.

5            In Embodiment 9, since a sulfonyl group included in the sultine exhibits polarity, the acid generated from the acid generator is held by the sulfonyl group in the resist film 602. Accordingly, the acid can be prevented from being deactivated in the exposed portion 602a of the resist film 602, so that the resist pattern 605 can be formed in a good shape.

#### 10    EMBODIMENT 10

A pattern formation method according to Embodiment 10 of the invention will now be described. Embodiment 10 is different from Embodiment 9 merely in using a negative chemically amplified resist material, and therefore, the chemically amplified resist material alone will be herein described.

15            Base polymer: poly((norbornene-5-methylenecarboxylic acid) – (maleic anhydride)) (wherein norbornene-5-methylenecarboxylic acid : maleic anhydride = 50 mol% : 50 mol%)    ...    2 g

Crosslinking agent: 1,3,5-N-(trihydroxymethyl)melamine    ...    0.4 g

Sultine: 3H-2,1-benzoxathiol=1-oxide    ...    0.07 g

20            Acid generator: triphenylsulfonium nonaflate    ...    0.05 g

Solvent: propylene glycol monomethyl ether acetate    ...    20 g

In Embodiment 9 or 10, the sultine is not limited to 3H-2,1-benzoxathiol=1-oxide.

Also, the mixing ratio of the sultine in the chemically amplified resist material is several wt% and may be appropriately changed.

25            Although the chemically amplified resist material used in each of Embodiments 1

through 10 includes one of lactone, a polymer including lactone, carbohydrate lactone, sultone and sultine, some of them may be included in the chemically amplified resist material.

Furthermore, in each of Embodiments 1 through 10, water or a nonaqueous  
5 solution of perfluoropolyether or the like can be appropriately used as the solution supplied onto the resist film. In the case where the exposing light is UV such as a g-line or an i-line, or deep UV such as KrF laser, ArF laser, Kr<sub>2</sub> laser, ArKr laser or Ar<sub>2</sub> laser, the solution is preferably water, and in the case where the exposing light is vacuum UV such as F<sub>2</sub> laser, the solution is preferably a nonaqueous solution.

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